COMPOSITION AND CHANGES IN ATMOSPHERIC DEPOSITION NEAR ATLANTA, GEORGIA, 1986-99

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Abstract. Trends in dry and wet deposition were investigated using data from a weekly sampling network at the Panola Mountain Research Watershed (PMRW), a forested research site 25 km, southeast of Atlanta, Georgia. Wet and dry atmospheric deposition has been monitored using various methods at PMRW since 1985, as a site of National Oceanic and Atmospheric Administration (NOAA) Atmospheric Integrated Monitoring Network (AIRMoN-dry) and following protocols of the National Trends Network (NTN). These data were compared for overlapping collection periods and analyzed for temporal trends. From 1986-99, the annual wet deposition of sulfur (S) and nitrogen (N) averaged 400 and 300 eq ha^{-1} (6.4 and 4.2 kg ha^{-1}), respectively. Inferential model estimates of annual dry S and N deposition from 1986-97 averaged 230 and 160 eq ha^{-1} (3.7 and 2.2 kg ha^{-1}), respectively. From 1993-99, net S deposition (dry deposition plus canopy interactions) for coniferous and deciduous throughfall (throughfall minus precipitation) averaged 400 and 150 eq ha^{-1} (6.8 and 2.3 kg ha^{-1}), respectively. The pH of precipitation is acidic, the volume weighted mean (VWM) pH (from H concentration) is 4.44 for 1986-99. Coniferous throughfall also is acidic having an annual volume-weighted mean VWM pH of 4.42 from 1993-99. The inferential model estimates are within this range and the variation in net S deposition of throughfall is attributed to variations in the leaf area index above the collectors and the representativeness of the collectors of throughfall for each canopy type. Temporal variations in precipitation SO_4 concentrations are similar to the atmospheric SO_4 concentrations, and are highest in summer and lowest in winter. In contrast, atmospheric SO_2 concentrations are negatively correlated with the atmospheric SO_4 concentrations. Atmospheric deposition trends were not detected for the entire sampling period, but were detected for shorter periods (four to five year). Annual S and N deposition increased from 1986 to 1990, decreased from 1991 to 1994, and increased from 1995 to 1999. The recent S and N deposition increase does not reflect the expected emission reductions associated with the January 1, 1995, implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments.

INTRODUCTION

Atmospheric deposition is a major source of chemical constituents to many ecosystems. The transfer occurs by three major pathways: (1) precipitation scavenging, in which particles are incorporated in hydrometeors and deposited in the resulting rain, snow, sleet or hail; (2) interception by fog and mist; and (3) dry deposition, in which large particles, aerosols and gases are removed by surfaces in the ecosystem. In the Atlanta, Georgia area, pathways (1) and (3) dominate, and the temporal and spatial variations in atmospheric deposition reflect variations in the constituent sources, transport from the source to the receptor, and deposition. Wet deposition can be monitored using a wet-only precipitation collector. Dry S and N deposition can be modeled using air quality and micrometeorology (Hicks and others, 1991). Also, total S deposition to a forest can be monitored by collecting throughfall, *i.e.*, water that travels through the forest canopy; dry S deposition at Panola Mountain Research Watershed (PMRW) can be determined by subtracting the wet deposition from the total S deposition (Cappellato and others, 1998). Expectations were that with the January 1, 1995, implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments, atmospheric sulfur (S) deposition would decrease in response to SO_2 emission reductions. This paper discusses atmospheric deposition at the PMRW (fig. 1), a forested watershed near Atlanta, to determine the relative contribution of wet and dry deposition to total atmospheric deposition and to evaluate temporal trends in the atmospheric deposition.

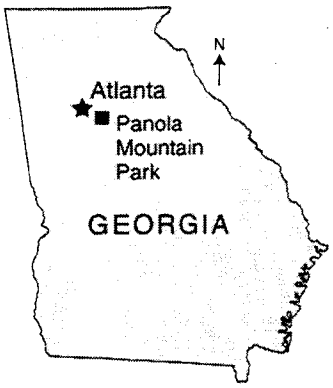

Figure 1. Panola Mountain State Conservation Park, near Atlanta, Georgia.

Methods

The 41-ha PMRW is about 25 km southeast of Atlanta, Georgia, in the Panola Mountain State Conservation Park and is one of five small watersheds of the USGS Water, Energy, and Biogeochemical Budgets Program (Baedecker and Friedman (2000); Peters and others, 2000). Deciduous and coniferous throughfall (1993-99) and wet deposition using National Atmospheric Deposition Program/National Trends Network (NADP/NTN) protocols (1985-99) were monitored weekly (Dossett and Bowersox, 1999). From August 1985 through November 1997, dry S and N deposition was monitored weekly by combining air concentrations from a filterpack with micrometeorological data in a resistance model (Hicks and others, 1991; Meyers and others, 1991). The site at PMRW is part of the National Oceanic and Atmospheric Administration (NOAA) AIRMoN-dry network (NOAA, 2000); dry deposition estimates will herein be called NOAA dry deposition.

Precipitation and throughfall were collected weekly from wet/dry precipitation collectors and analyzed for major ion concentrations. Amounts of precipitation and throughfall were determined by the volume collected and the collector area. Major solutes (Na, K, Ca, Mg, NH_4, Cl, NO_3, and SO_4) were determined by ion chromatography prior to 1991. Since 1991, the cations—Na, K, Ca, and Mg—are determined by direct current plasma on a filtered (0.45 μm) acidified aliquot, and NH_4 is determined colorimetrically using salicylate hypochlorite.

Individual solute deposition in precipitation was computed by multiplying the solute concentration by the rainfall or throughfall amount. The Kendall test (Gilbert, 1987), a nonparametric test, was used to determine if changes in annual deposition were increasing or decreasing.

RESULTS AND DISCUSSION

Precipitation and wet deposition

For calendar years 1986-99, annual precipitation at PMRW averaged 1,225 mm and ranged from 860 mm in 1987 to 1,580 mm in 1994. Monthly precipitation ranged from 5 mm in June 1990, to 455 mm in July 1994, a result of tropical storm Alberto. The cation composition (Na, K, Ca, Mg, NH_4, and H) of precipitation is dominated by H (~50 percent) and NH_4 (~20 percent), and the anion composition (Cl, NO_3, and SO_4) is dominated by SO_4 (>50 percent) and NO_3 (~25 percent). Precipitation is acidic with the annual pH (from H concentration) averaging 4.44 and ranging from 4.21 to 4.66; the pH of weekly samples, however, was more variable ranging from 3.29 to 6.37 with the lowest pH values generally found in the lowest-volume samples. Deposition, and cation and anion composition varied seasonally—the seasons were divided into sequential 3-month periods with March–May for spring; June–August for summer; September–November for fall; and December–February for winter (fig. 2). The highest H (lowest pH) and SO_4 deposition typically were during the summer and spring. Summer SO_4 deposition was more than three times the winter deposition, which was the season for the lowest deposition of any solute. Na and Cl deposition varied the least among seasons, but even for these solutes, summer deposition was 2.0 and 1.3 times the winter deposition, respectively. The pH of precipitation is controlled primarily by the concentrations of SO_4 and NO_3; the r^2 of a linear regression of H concentration on SO_4 was higher than on NO_3 (0.91 and 0.73, respectively). The stronger association with SO_4 compared to NO_3 concentrations reflects the concentrations in precipitation, that is SO_4 dominates NO_3 by a factor of two and the annual averages were 36 and 16 $\mu eq\ l^{-1}$, respectively. Individual solute concentrations were highest in the lowest-volume samples, reflecting the concentrating effect of washout from the atmosphere. However, relations between solute concentration and rainfall are not statistically significant ($p<0.05$) and display considerable heteroscedasticity, having the largest concentration variance during weeks with the lowest rainfall.

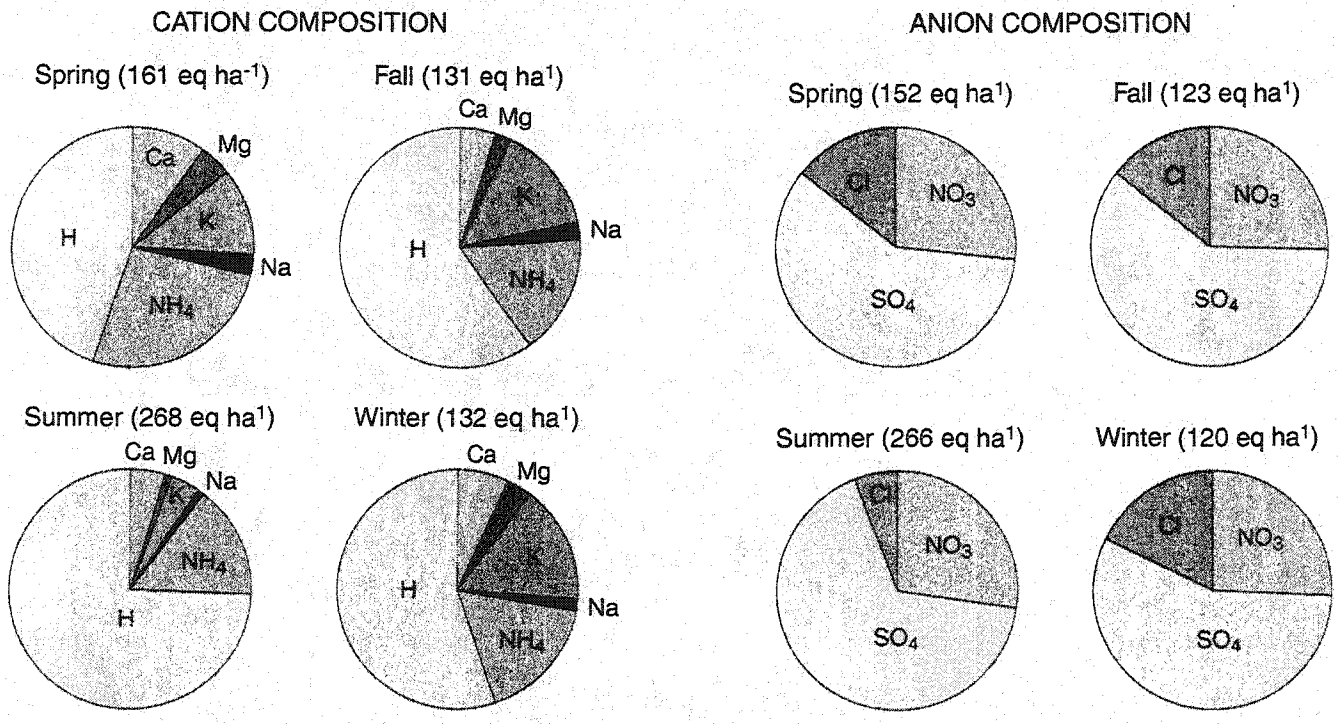

Figure 2. Seasonal cation and anion composition of wet atmospheric deposition at the Panola Mountain Research Watershed near Atlanta, Georgia, 1986–99. The average seasonal cation and anion deposition is given in parentheses.

Air quality and NOAA dry S and N deposition

Air concentrations of S and N species, measured with the filterpack, were positively skewed, *i.e.*, with most of the weekly values less than the mean. Consequently, median concentrations are reported to represent the populations. SO_2 concentrations varied seasonally, with high concentrations in winter and low concentrations in summer; the highest median SO_2 concentration (8.2 μg m^{-3}) was in February and the lowest (3.2 μg m^{-3}) was in August. In contrast, SO_4 concentrations were low in winter and high in summer—the lowest median weekly SO_4 concentration (2.8 μg m^{-3}) was in December and the highest (8.8 μg m^{-3}) was in July. The variation reflects the more rapid conversion of SO_2 to SO_4 under warmer conditions in summer; during the study period, median-monthly air temperatures at PMRW ranged from 5.9 ° C in January to 25.6 ° C in July. The SO_4 concentration of precipitation varied seasonally and was similar to and probably related to atmospheric SO_4 concentrations through aerosol washout during rainstorms. In contrast to SO_4, aerosol NO_3 concentrations were low, and varied seasonally with high median-monthly concentrations in spring (0.24 μg m^{-3}) and low concentrations in summer (0.08 μg m^{-3}). The HNO_3 concentrations were higher than aerosol NO_3 and were less variable seasonally than the other N and S species; the highest median concentration was 1.6 μg m^{-3} in March and the lowest was 1.2 μg m^{-3} in November.

The annual dry S (SO_4 plus SO_2) and N (HNO_3 plus NO_3) deposition averaged 230 and 160 eq ha^{-1} (3.7 and 2.2 kg ha^{-1}), respectively. The annual N deposition was highly correlated with the S deposition (r = 0.95). Weekly NOAA dry SO_4 deposition varied seasonally (fig. 3) having the same pattern as the air concentrations. The SO_2 deposition was more variable throughout the year compared to SO_4 (fig. 3). The NOAA SO_2 deposition is sensitive to surface wetness and temperature; surface wetness varies markedly throughout the year, which may explain the high variability in SO_2 deposition. Seasonal variations in N species deposition were not as pronounced as those for the S species (fig. 3). The highest deposition for both HNO_3 and NO_3 occurred in late winter and spring and the lowest in summer, which is comparable to the variations in SO_2 concentrations and deposition.

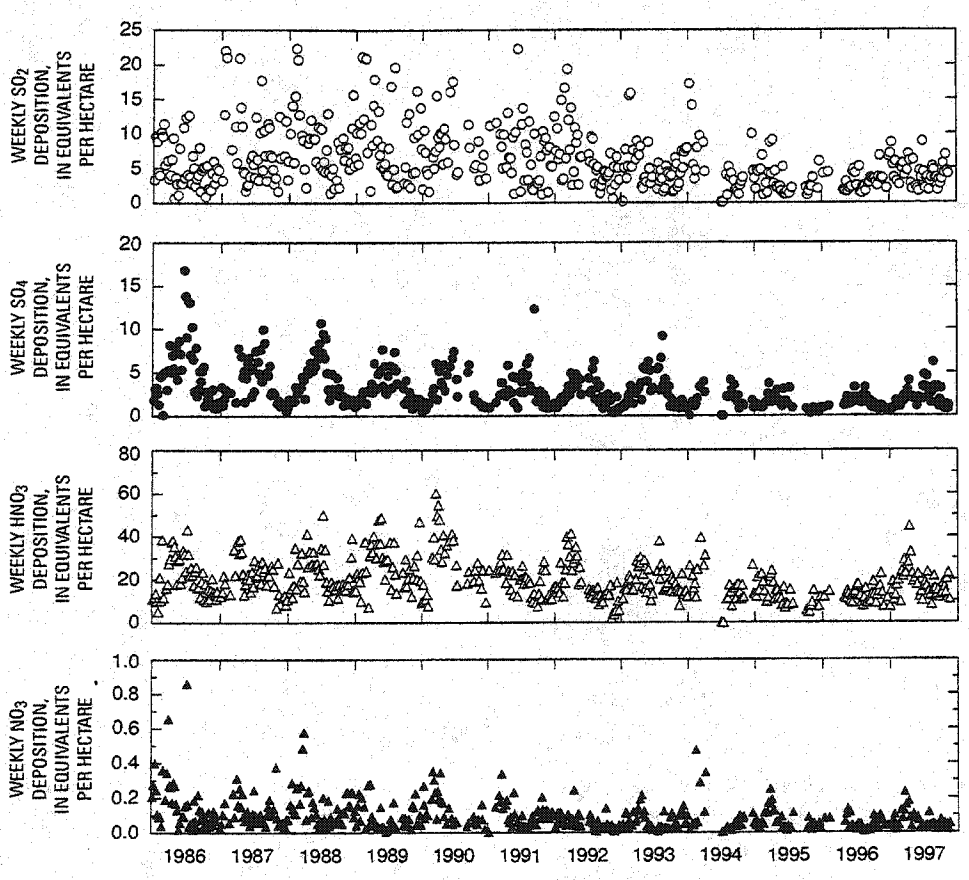

Figure 3. Weekly dry S and N deposition for 1986–97, estimated by combining weekly air concentrations from a filterpack and hourly micrometeorology in a resistance model.

Throughfall estimates of dry S deposition

From 1993-99, net S deposition (dry deposition plus canopy interactions) for coniferous and deciduous throughfall (throughfall minus wet deposition) averaged 400 and 150 eq ha^{-1} (6.8 and 2.3 kg ha^{-1}), respectively. The differences are attributed to variations in the leaf area index (LAI, leaf surface area per unit land surface area) above the collectors and the representativeness of the throughfall collectors for each canopy type. LAI was not measured and representativeness was not evaluated. During the same collection period as that of the throughfall, the wet S deposition averaged 350 eq ha^{-1} (6.0 kg ha^{-1}). The dry S deposition estimated from the throughfall S mass balance, therefore, ranges from 30 to 53 percent. In a mass-balance study of dry S deposition for a 500-mi^2 lichen and moss covered bedrock outcrop at PMRW, Peters (1989) reported that 30 percent of the total atmospheric S deposition to the outcrop was dry deposition, which is similar to the results presented herein. The lower estimate for the outcrop (Peters, 1989) and for the deciduous throughfall, probably reflects a lower LAI; and hence, a low filtering of atmospheric constituents of the respective canopies. From a rainstorm-based S cycling study at PMRW conducted from October 1987 to November 1989, Cappellato and others (1998) estimated the dry S deposition to be about 42 percent of the total atmospheric S deposition to the deciduous and coniferous forests.

Temporal trends in annual deposition

Trends in the annual wet deposition of H, SO_4, and NO_3 from 1986 to 1999 were not statistically significant (fig. 4). Deposition trends for these solutes, however, are statistically significant for shorter periods; SO_4, and NO_3 increased from 1985 to 1990 ($p < 0.01$), H, SO_4, and NO_3 decreased from 1991 to 1994 ($p<p0.05$), and H, SO_4, and NO_3 increased from 1995 to 1999 ($p<0.01$ for SO_4, and NO_3 and $p<0.05$ for H). Concentrations and deposition of H, SO_4, and NO_3 were lowest in 1994. The increasing trends in solute deposition since 1995 are of interest because atmospheric S deposition was expected to decrease due to SO_2 emission reductions associated with the January 1, 1995,

implementation of Phase I of Title IV of the 1990 Clean Air Act Amendments. No trends were detected in rainfall amount. The SO_4 concentration and deposition are highly correlated with NO_3 (>0.99), and H is highly correlated with SO_4 plus NO_3 (>0.96).

The annual total deposition, as measured by weekly throughfall, increased significantly after 1994 to the coniferous forest for SO_4 and H ($p<0.05$), and to the deciduous canopy for H ($p<0.01$). A trend in annual dry deposition (throughfall minus wet deposition) was not detected for any solute; this may be due to the imprecision of this method for estimating dry deposition.

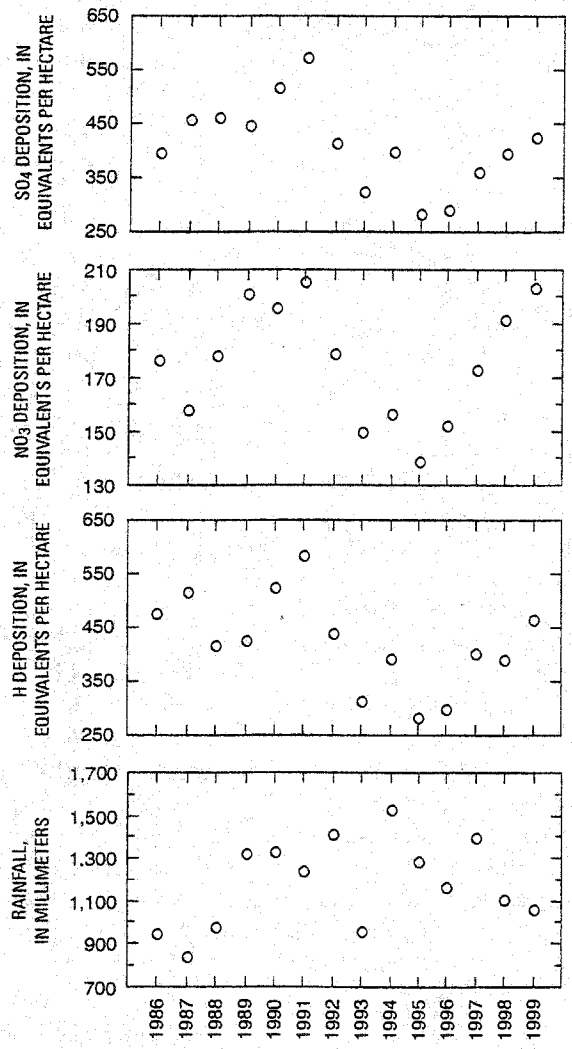

Figure 4. Temporal trends in annual SO_4, NO_3, and H wet deposition and rainfall at the Panola Mountain Research Watershed, near Atlanta, Georgia, 1986–99.

LITERATURE CITED

Baedecker, M.J. and Friedman, L.C., 2000, Water, Energy, And Biogeochemical Budgets, A Watershed Research Program. U.S. Geological Survey Fact Sheet 165-99.

Cappellato, Rosanna, Peters, N.E., and Meyers, T.P., 1998, Above-ground sulfur cycling in adjacent coniferous and deciduous forests and watershed sulfur retention in the Georgia piedmont, USA: Water, Air and Soil Pollution, v. 103, nos. 1-4, p. 151-171.

Dossett, S.R., and Bowersox, V. C., 1999, National Trends Network Site Operation Manual: Champaign, Ill., National Atmospheric Deposition Program Office, Illinois State Water Survey, NADP Manual 1999-01.

Gilbert, R.O., 1987, Statistical methods for environmental pollution monitoring: New York, Van Nostrand Reinhold, 250 p.

Hicks, B.B., Hosker, R.P., Jr., Meyers, T.P., and Womack, J.D., 1991, Dry deposition inferential measurement techniques I—Design and tests of a prototype meteorological and chemical system for determining dry deposition: Atmospheric Environment, v. 25A, no. 10, p. 2345-2359.

Meyers, T.P., Hicks, B.B., Hosker, R.P., Womack, J.D., and Satterfield, L.C., 1991, Dry deposition inferential measurement techniques, II—seasonal and annual deposition rates of sulfur and nitrate: Atmospheric Environment, v. 25A, no. 10, p. 2361-2370.

Peters, N.E., 1989, Atmospheric deposition of sulfur to a granite outcrop in the Piedmont of Georgia, U.S.A. *in* J.W. Delleuer (*ed.*): Atmospheric Deposition, IAHS Publication 179, p. 173-181.

Peters, N.E., Hooper, R.P., Huntington, T.G., and Aulenbach, B.T. 2000, Panola Mountain Research Watershed—Water, Energy, and Biogeochemical Budgets Program. U.S. Geological Survey Fact Sheet 162-99.

NOAA, 2000, Program: The Atmospheric Integrated Monitoring Network (AIRMoN). **http://www.arl.noaa.gov/research/programs/airmon.html** [*accessed February 20, 2001*].